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PREPARATION OF N-(ALKENYLOXYMETHYLENE) ACRYLAMIDE COPOLYMERS AND PRODUCTS THEREOF

Karl Dinges, Cologne-Stammheim, and Erwin Müller, Leverkusen, Germany, assignors to Farbenfabriken Bayer Aktiengesellschaft, Leverkusen, Germany, a German corporation

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The present invention relates to polymers and copolymers containing methylol ether groups and a process for production of said polymers.

The production of polymers and copolymers of polymerisable organic compounds which contain the grouping

I. $$-CO-N(R_x)-CH_2-OR_y$$

and wherein R_x represents hydrogen or alkyl and R_y represents alkyl (i.e., a saturated aliphatic hydrocarbon radical), is already known. As compounds of the said type, there are more especially described acrylic and methacrylic methylol alkyl ethers, such as for example the methyl or ethyl ethers. Using this process, it is possible to produce polymers containing unbranched methylol alkyl ether groups, which polymers can be cross-linked in a second stage by the action of hydrolysing agents, such as acids, at elevated temperature. This cross-linking takes place in the presence of hydrolysable agents, advantageously above 100° C., whereas cross-linking temperatures up to 150° C. are necessary in the absence of hydrolysing agents such as acids. The products thus obtained are synthetic resins or elastomers, which are suitable for various purposes of use in the plastics art.

The process according to the present invention consists in the production of homopolymers and copolymers of methylol alkenyl ethers of polymerisable organic acid amides, i.e., compounds which contain in addition to at least one polymerisable carbon to carbon double bond, the grouping

II. $$-CO-N(R_1)-CH_2-OR_2$$

in which the radical R_1 represents a hydrogen atom, a saturated monovalent aliphatic hydrocarbon radical with 1–5 carbon atoms, preferably a methyl or ethyl radical, and R_2 represents an alkenyl radical (i.e., monoolefinically unsaturated aliphatic radical) having up to 6 carbon atoms, advantageously a radical containing 3 carbon atoms. The grouping represented by the foregoing formula and hereinafter referred to as an alkenyl methylol ether grouping, should be present at least once in the molecule to be polymerised.

Compounds of this type can be polymerised as such or admixed with one or more organic compounds which contain at least one polymerisable carbon to carbon double bond, in block, solution or emulsion, to form compounds of high molecular weight containing methylol alkenyl ether groups. These compounds can be cross-linked at elevated temperature or with hydrolysing agents, more especially acids or poly-functional compounds which are able to react with the methylol ether groups or their cleavage products which form under the action of hydrolysing agents.

As typical examples of these methylol alkenyl ethers there are to be mentioned N-(allyloxymethylene)-acrylamide and -methylacrylamide, which can be obtained from the corresponding methylol compounds by etherification with allyl alcohol in acid medium.

III. $$CH_2=C(CH_3)-CO.NH.CH_2-O-CH_2-CH=CH_2$$

IV. $$CH_2=CH-CO-NH-CH_2-O-CH_2-CH=CH_2$$

Furthermore compounds as for example

N-(allyloxymethylene)-N-methyl-methacrylamide,
N-(allyloxymethylene)-N-ethyl-methacrylamide,
N-(allyloxymethylene)-N-propyl-methacrylamide,
N-(allyloxymethylene)-N-methyl-acrylamide,
N-(allyloxymethylene)-N-ethyl-acrylamide,
N-(allyloxymethylene)-N-propyl-acrylamide.

It is surprising that such compounds which contain two carbon-to-carbon double bonds can be transformed into unbranched polymers or copolymers by the fact that under the conditions of the present procedure only the double bond juxtaposed to the carbonyl group polymerises. The thus formed polymer is a thermoplastic product of high molecular weight which can be stored without any modification at room temperature, in aqueous solution or aqueous emulsion, while still containing reactive methylol alkenyl ether groupings which are available for further cross-linking and polymerisation reactions.

In accordance with the present process, both homopolymers and copolymers can be prepared with the use of the aforementioned special monomers. Copolymers can contain any desired proportions of the components to be used according to the invention, i.e., from about 0.5–99 mol percent (calculated on the total amount of monomers), but contents of 1–15 mol percent are of particular interest.

Suitable as copolymerisable monomers for the production of copolymers by the present process are the various types of organic compounds with one or more polymerisable carbon-carbon-double bonds, advantageously those with one or two conjugated double bonds.

To be mentioned are: polymerisable organic compounds having a terminal $CH_2=CH-$ group, as for example: acrylic or methacrylic acid as well as their esters with saturated monohydric aliphatic alcohol or methacrylic acid amide, acrylonitrile and methacrylonitrile, aromatic monovinyl compounds, i.e., styrenes which are halogenated or alkylated on the nucleus or side chains, such as α-methyl styrene, vinyl toluene and chlorostyrene, styrene derivatives, vinyl halides such as vinyl chloride, vinylidene chloride, vinyl esters such as vinyl acetate, vinyl propionate, vinyl butyrate, and vinyl ketones and vinyl ethers, such as methyl vinyl ether. Furthermore of a preferred interest are open chain aliphatic conjugated diolefines with 4–6 carbon atoms, such as butadiene, chloroprene, isoprene and 2,3-dimethylbutadiene.

Furthermore, monomers with a cross-linking action and containing at least two non-conjugated (isolated) carbon-carbon double bonds can also be used as copolymerisation compounds in quantites of about 0.01 to 10% by weight, based on the weight of the total monomers, such as for example glycol diacrylates, glycol dimethacrylates, allyl acrylate and/or methacrylate, divinylbenzene or substitution products of the said compounds.

It is obviously possible that other unsaturated polymerisable compounds with self cross-linking groups can also be used as copolymerisation component. Mentioned as examples of suitable copolymerisable components of this nature which permit the introduction of self cross-linking groupings are the methylol ethers of acrylic or methacrylic acid amides of the following general Formula

V. $$CH_2=C(R)-CO-N(R_1)-CH_2OR_2$$

in which R stands for hydrogen or methyl, R_1 for hydrogen, alkyl, aralkyl or aryl, R_2 for alkyl or cycloalkyl, such